

Abstract

The comprehension of the dynamics characteristics of the polyelectrolyte solutions has industrial and biological interest and it plays an important role for the interpretation and the control of their properties. On account of that, molecular dynamics simulations are employed in systems of dendrimer solutions of explicit solvent and monovalent counterions, below the dendrimer overlap concentration. Systems of two different dendrimer generations – third (G3) and fourth (G4) – are examined with charged terminal groups in order to explore aspects of the static and dynamic behavior of the dendrimers and counterions. The dendrimer molecules are presented as bead-spring, united atom models, while counterions and solvent as interacting beads. During the variation of the strength of electrostatic interactions and the dendrimer concentration/total volume fraction static properties, such as radius of gyration, pair distribution functions and static structure factor, and dynamic properties, by means of mean square displacements, reorientation of bonds, core-to-shell vectors, Van Hove functions (self and collective motion), “survival time” correlation function and incoherent dynamic structure factor, are examined.

The results of this study reveal that an ordering of dendrimers polyelectrolytes (formation of crystalline phases) can be achieved by controlling the Coulombic interactions, while characteristic regimes can be distinguished depending on these kinds of interactions. At high Bjerrum lengths an effective overcharging of dendrimer molecules and counterion condensation is noted, as well as a characteristic slow-down of the dendrimer motion similar to that expected from a glasslike transition. A similar slow-down is observed to the counterion diffusional motion upon increase of the Coulombic interactions and simultaneously a development of dynamic heterogeneities in counterion self-motion. The result of the present thesis may serve as a step forward towards the description of the mechanisms pertinent to ion migration in macroion dispersions and the ionic motion in a broader range of polyelectrolyte systems (e.g. globular proteins, spherical brushes).